Crosscutting Applications for a New Class of Ultra-Hard Materials Based on $AlMgB_{14}$

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OIT - Industrial Materials for the Future

The Problem

Current-generation hard materials employed in metal casting, mining, agriculture, and forest products industries are operating at or near their performance limits.

Advances in in cutting/grinding/machining speed (efficiency), range of applications, energy savings, and environmental impact minimization will not be realized unless new materials are developed

Solution:

A new family of ultra-hard materials based on $AlMgB_{14}$

- **hardness from 28 - 46+ GPa,**
- **good fracture toughness,**
- **chemical compatibility with a wide range of workpiece materials,**
- **relatively low cost**
- **excellent potential for “self-lubricating” coatings**

The Challenge

- Identify & quantify fundamental mechanisms responsible for extreme hardness
- Optimize hardness, toughness, wear resistance
- Develop appropriate mechanisms to promote high temperature oxidation resistance
- Processing scale-up (grams $\rightarrow$ Kg)
- Identify key industrial benefactors of the technology
- Provide technical assistance to commercialization efforts

Summary of Technology Status

Limitations with all existing competing technologies:

1) **low hardness**

   silicon carbide, alumina, tungsten-carbide

2) **low hot hardness**

   sintered tungsten-carbide, high strength steels, cubic boron nitride, titanium carbide

3) **poor wear resistance/chemical inertness**

   sintered tungsten-carbide, cermets (titanium carbide, titanium nitride), high strength steels, diamond (when used on iron or nickel-containing alloys)

4) **low fracture toughness**

   ceramics (alumina, silicon nitride)

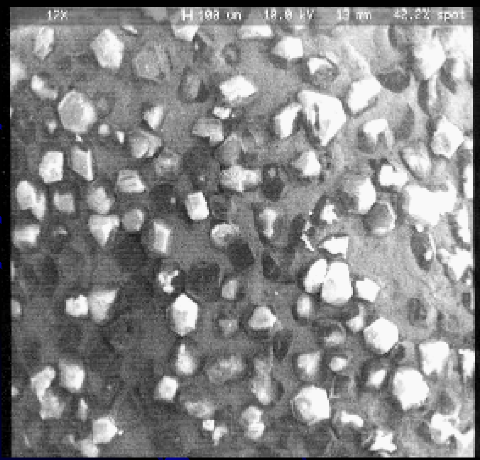
5) **high cost**

   diamond, cubic boron nitride

Problems with existing technology

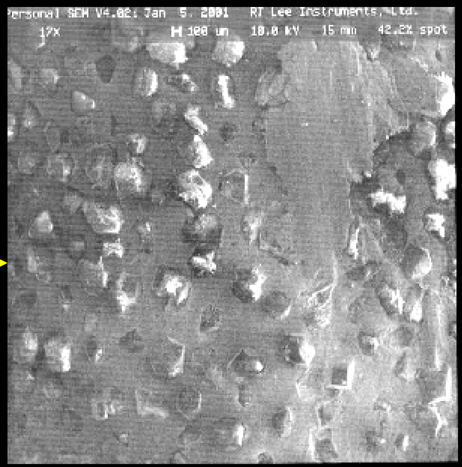
- **diamond, c-BN are expensive ($1,000 - $5,000/lb.)**
- **diamond reacts with iron (steels) during machining/cutting**
  - reaction forms an undesirable by-product
  - reaction is exacerbated by high temperatures during machining
    - diamond is unsuitable for high speed cutting of iron-based materials
    - 90 million tons of iron & steel are machined each year in the U.S.,
    - higher cutting speeds $\Rightarrow$ direct cost savings

Example: failure of diamond grit during low-speed machining of steel



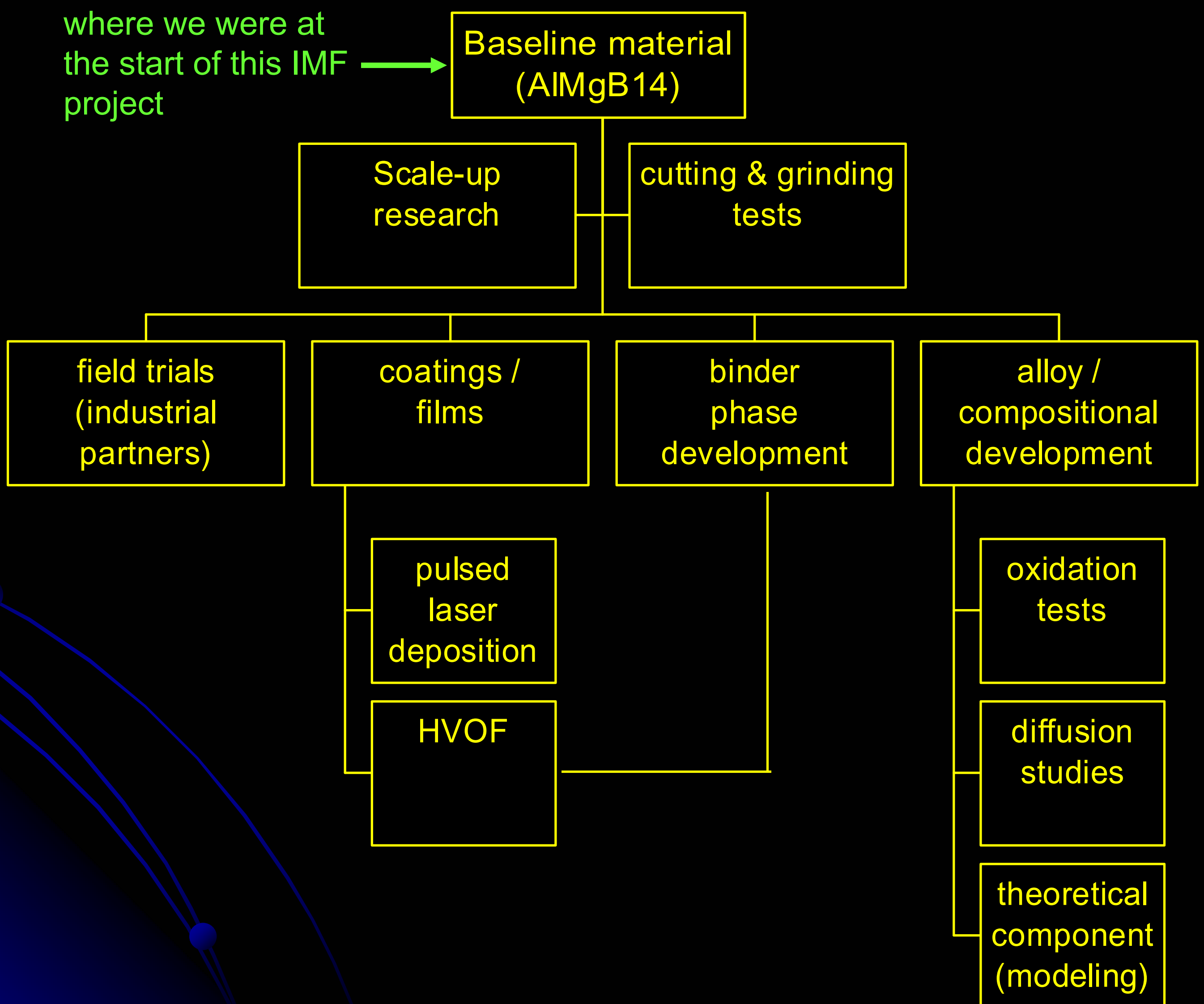
Diamond grit before cutting 304 SS

~ 3 min.



Diamond grit after cutting 304 SS

Project growth during OIT sponsorship:

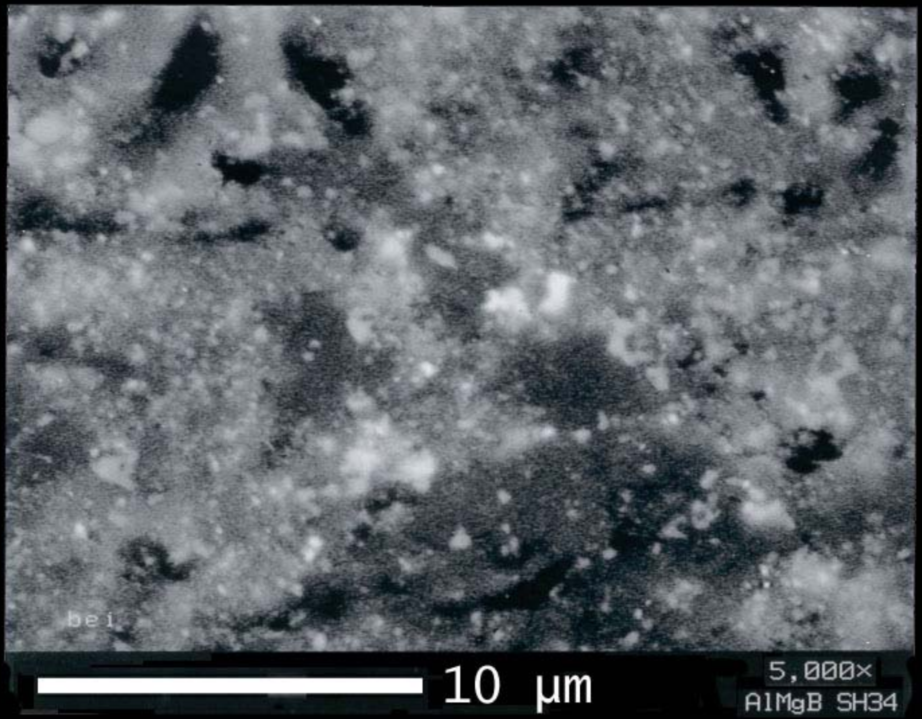


<u>Active</u> Industrial Collaborators as of June, 2003

- Praxair Surface Technologies
- Kennametal Adv. Solutions Group
- Kennametal - Corporate
- Norton-St. Gobain
- A&H Industries
- Primewood / E&W Tooling
- Advanced Ceramics, Inc.
- Engis Corp.
- Union Electric Steel
- Concurrent Technologies
- Harris Corporation
- Stellram
- Sunnen Products Co.

Extreme hardness requires:

- hard matrix phase
- ultra-fine microstructure
  - uniform distribution of nanoscale second phase (TiB_2)
- low oxygen content
- no porosity



Processing objective: a high energy, high capacity mechanical alloying approach leading to reproducible microstructures in Kg quantities

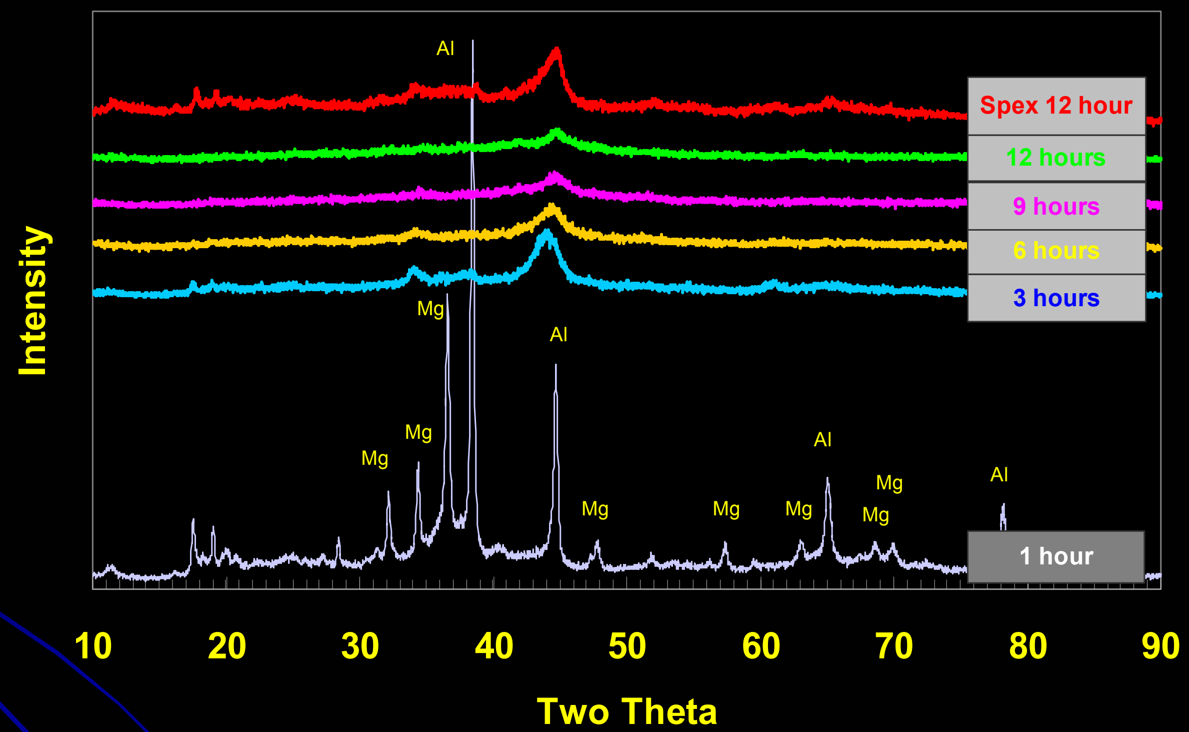
Processing scale-up

Solid state synthesis (MA)

- Critical component - enabling technology

Characterization of Zoz-milled powder

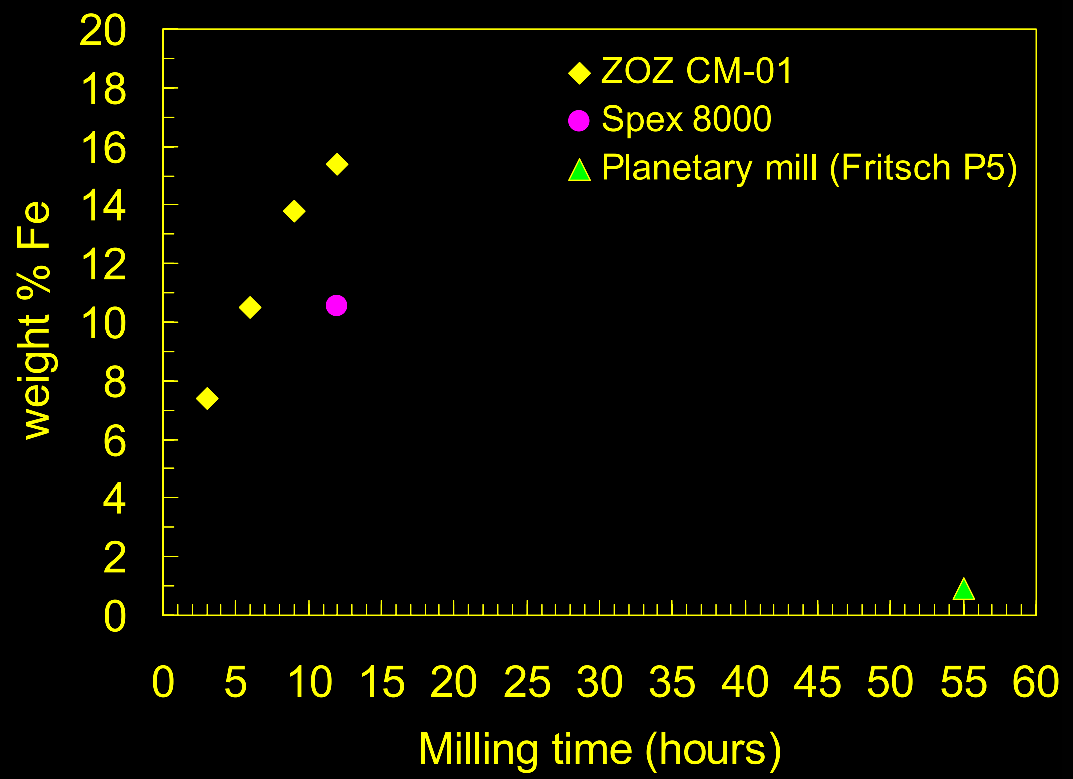
I. Comminution behavior:



- significant particle size reduction between 1 and 2 hours
- 3 hour processing in CM-01 produces material comparable to 12 hour processing in Spex 8000.

Characterization of Zoz-milled powder

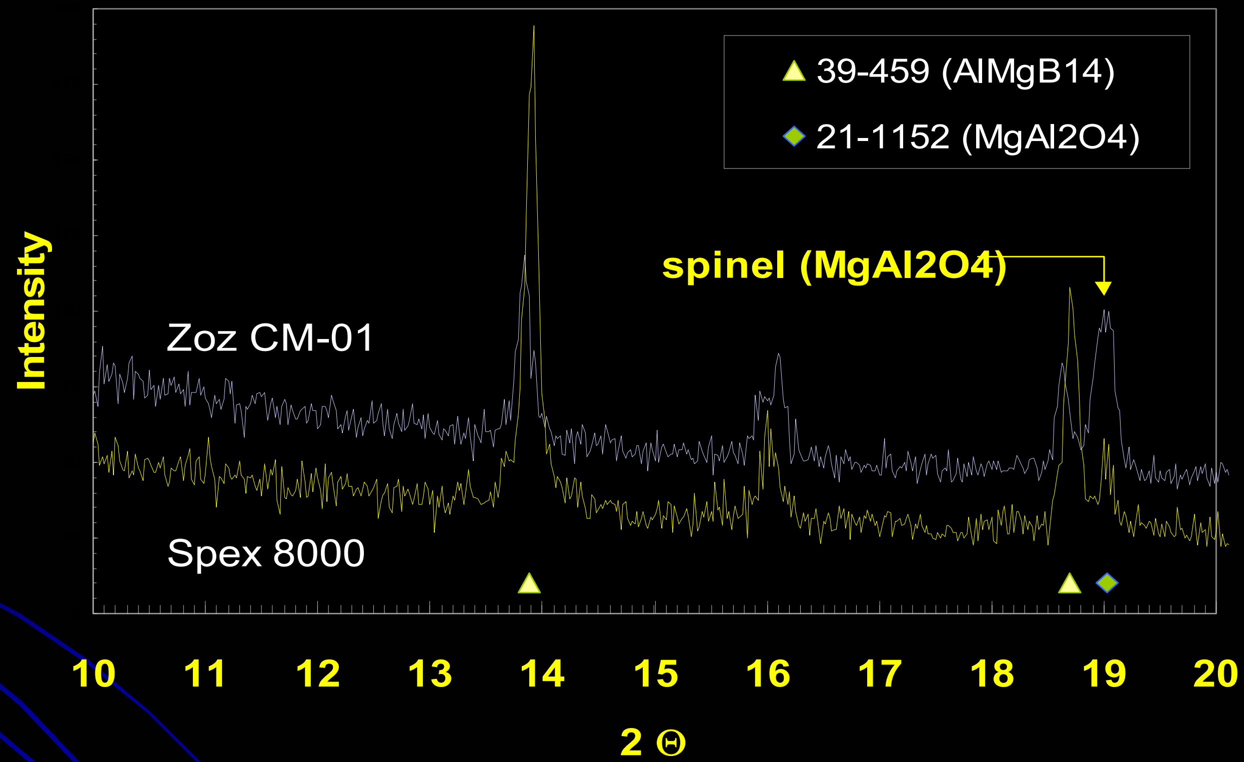
II. Fe pick-up from wear debris: (determined by ICP)



- Fe-content is a function of impact energy
  - Lowest contamination from PM; highest from Zoz CM-01
- Small amount of Fe desirable; in-situ toughening mechanism

Characterization of Zoz-milled powder

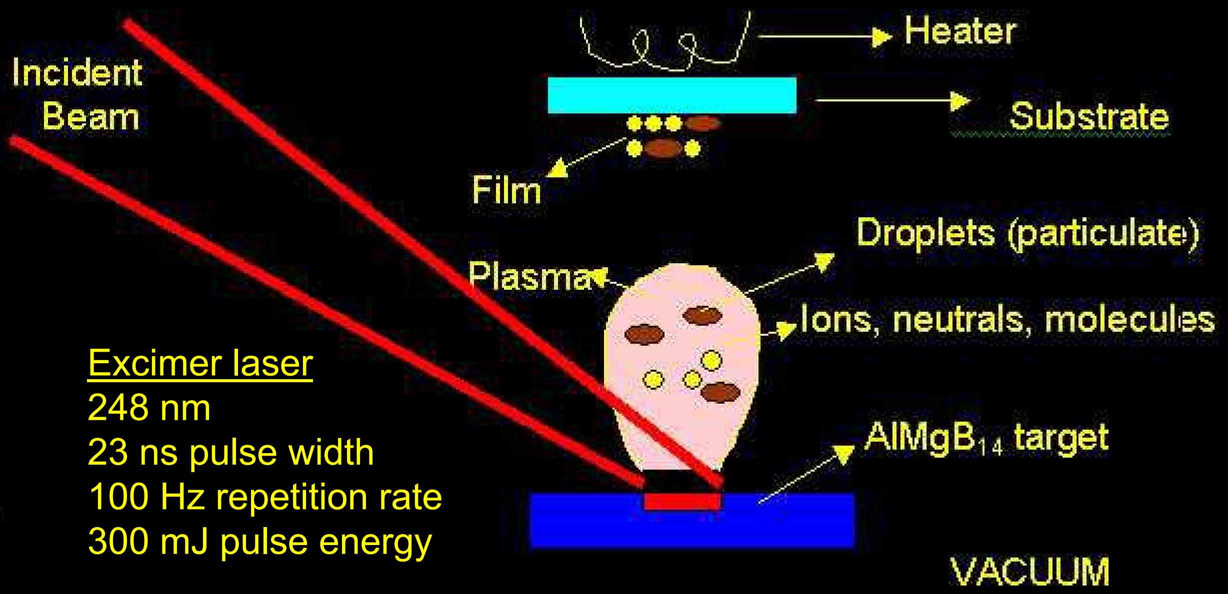
III. Hot-pressed compacts:



- **Both approaches produce desired 1:1:14 phase**
- **Increased levels of spinel (impurity phase) observed in Zoz-milled samples**
    - consequence of imperfect design of powder charging / discharging design
    - recently engineered a modification to reduce oxygen exposure

Thin films/coatings

- Original proposal - thermal spray (HVOF)
  - Typically requires kilogram quantites of feed powder
  - Needed alternative coating approach for research-scale sample sizes
- Pulsed Laser Deposition (PLD) employed during completion of scale-up efforts (Zoz mill)

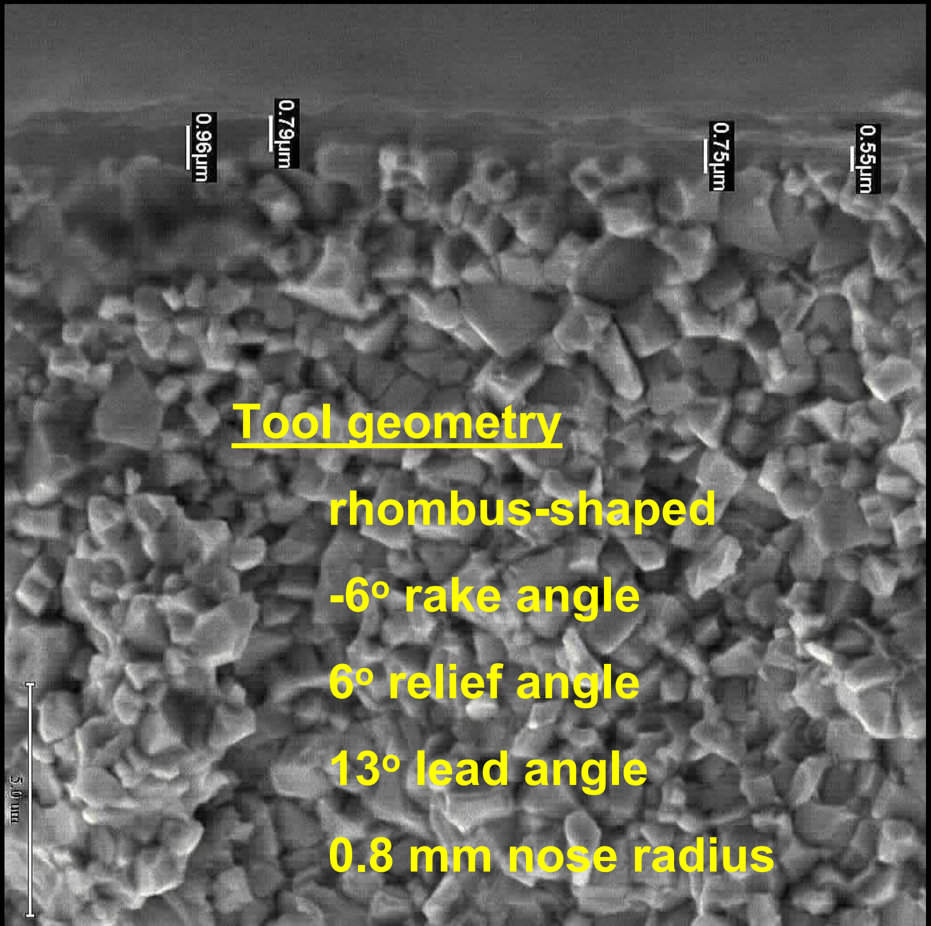


Thin films/coatings

- **Initial deposition on WC-6%Co cutting tools**
  Carboloy-Seco Grade 883 1 micron grain size (CNMG 432-MR4)
  (recommended for Ti machining)

$AlMgB_{14}$ coating →
(average thickness ~ 700 nm)

WC/Co substrate →



Tool geometry

rhombus-shaped

-6^o rake angle

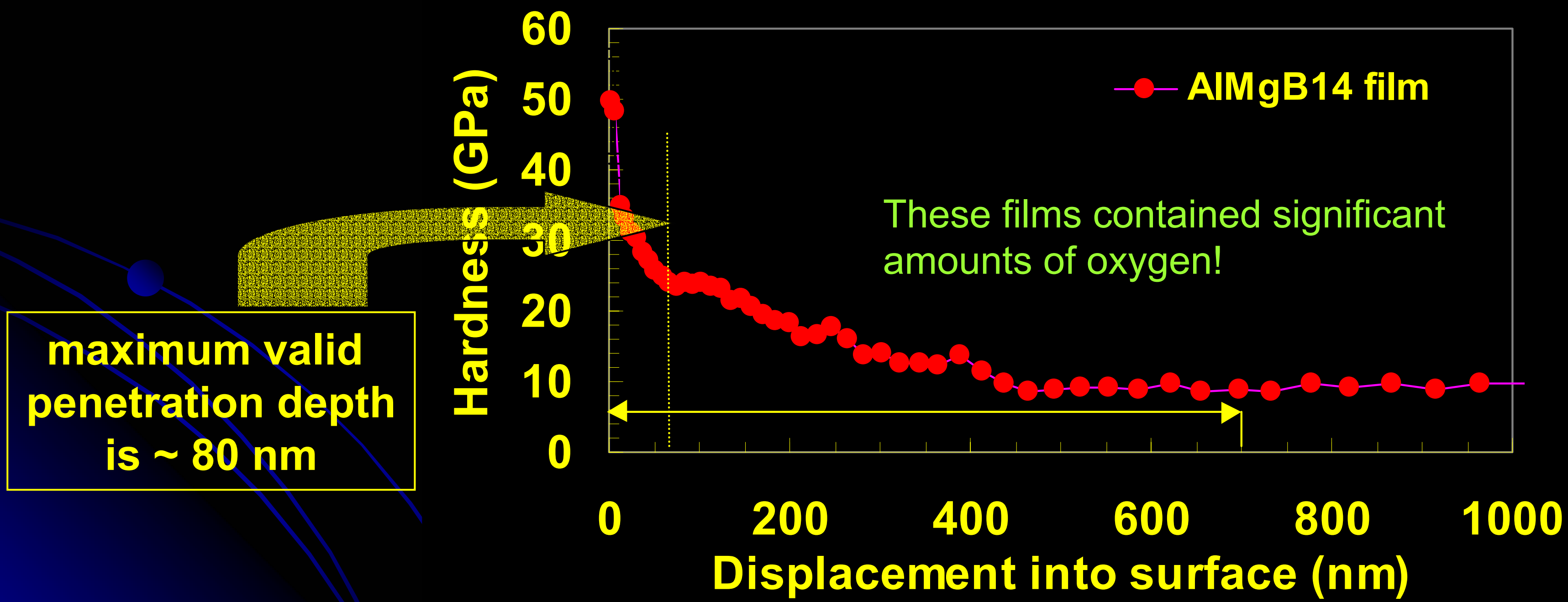
6^o relief angle

13^o lead angle

0.8 mm nose radius

Thin films/coatings

- Initial coatings were characterized and tested "as-deposited"
  - as-deposited film is amorphous
  - heat treatment promotes growth of 1:1:14 phase

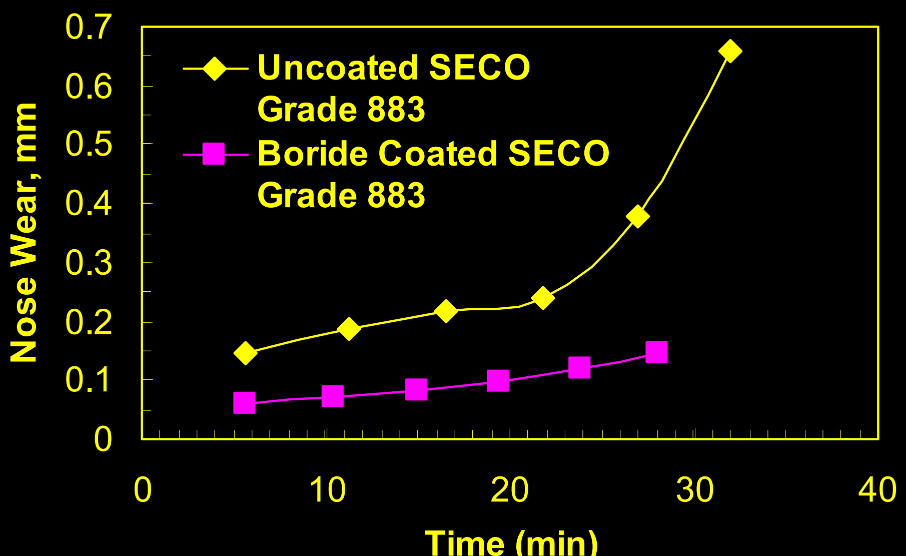


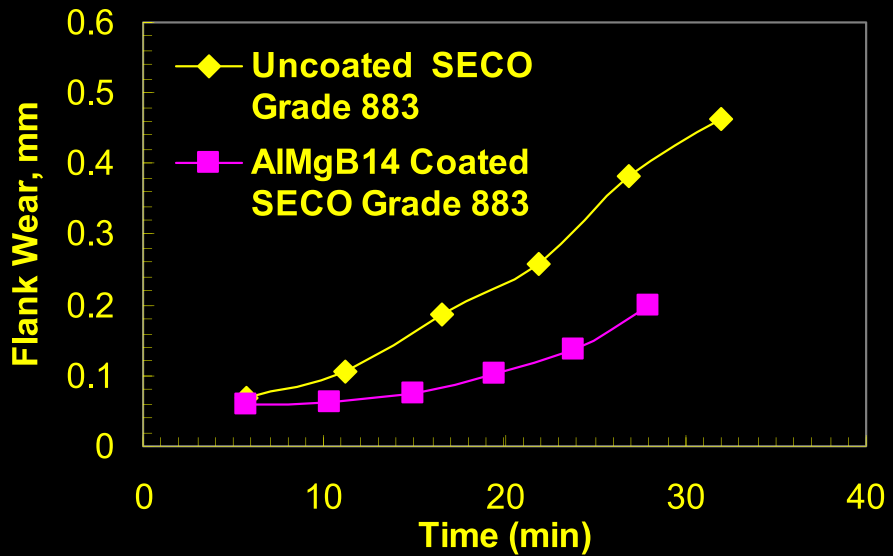
Film hardness ~ 22 - 25 GPa, WC/Co substrate hardness ~ 13 GPa

lathe cutting tests: Ti-6Al-4V

These results were obtained with "low" hardness, amorphous 1:1:14 coatings containing excessive spinel impurity phase

Special thanks to P. Molian and R. Cherukuri from Iowa State University's Dept. of Mechanical Engr. for conducting these cutting tests.



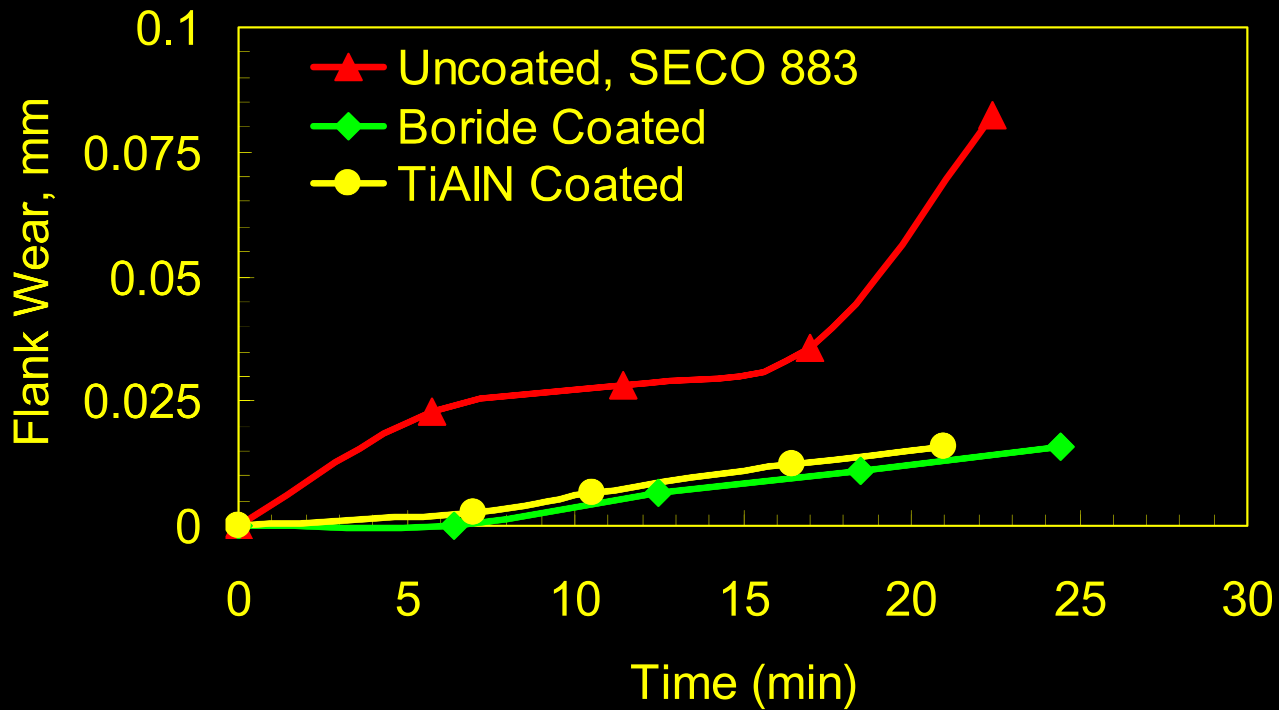


lathe cutting tests: Ti-6Al-4V

comparison with other potential technologies

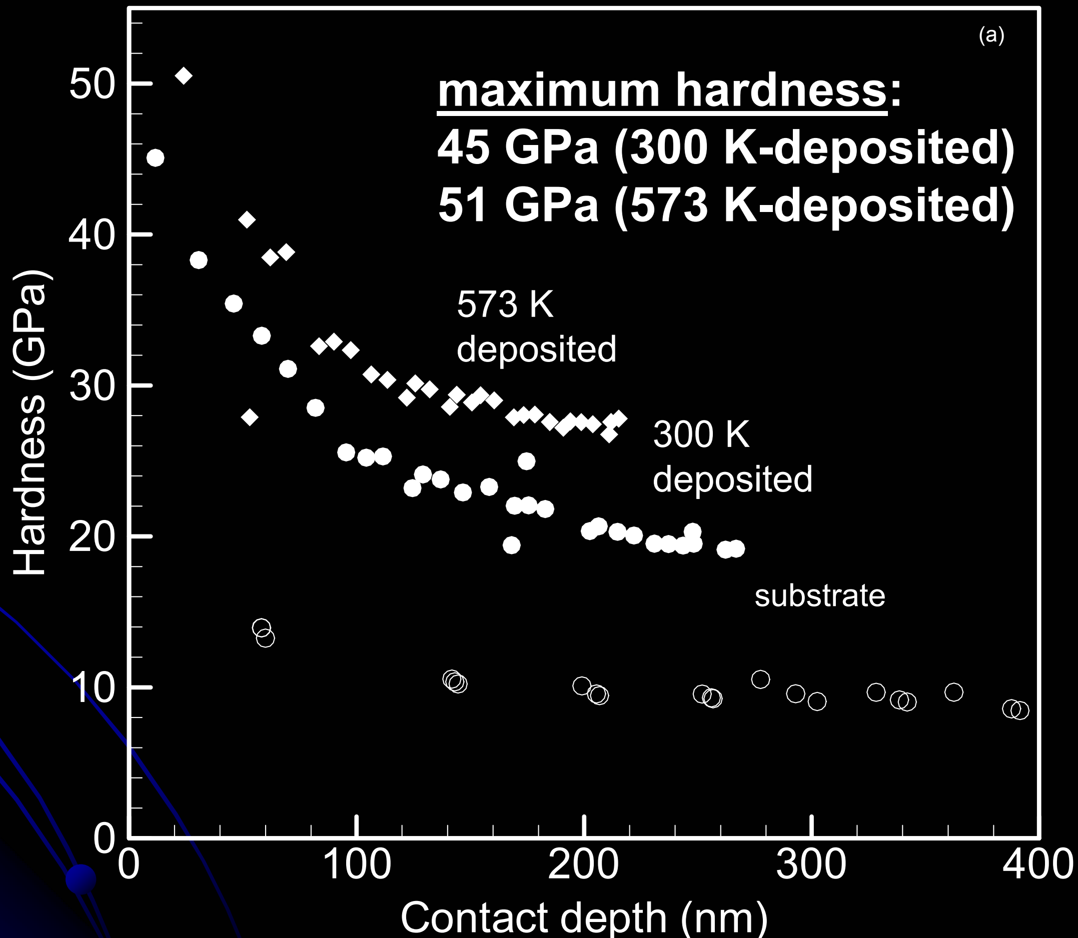
Flank wear:

uncoated, ultra-hard boride coated, and state-of-the-art PVD-coated TiAlN carbide tools:



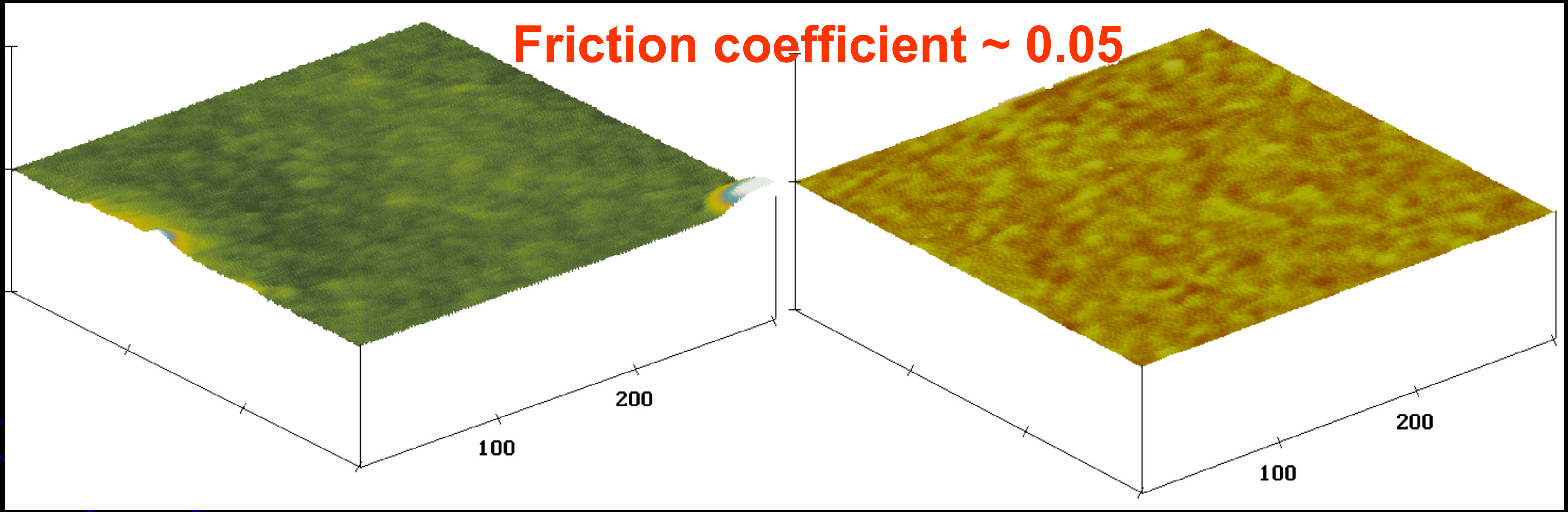
Thin films/coatings (baseline material)

- PLD studies repeated under improved vacuum conditions (10^{-7} Torr vs. 10^{-4} Torr)



Thin films/coatings

AFM images (0.3 × 0.3 μm^2) of (a) the 293K -deposited $AlMgB_{14}$ film and (b) the 573 K-deposited $AlMgB_{14}$ film.



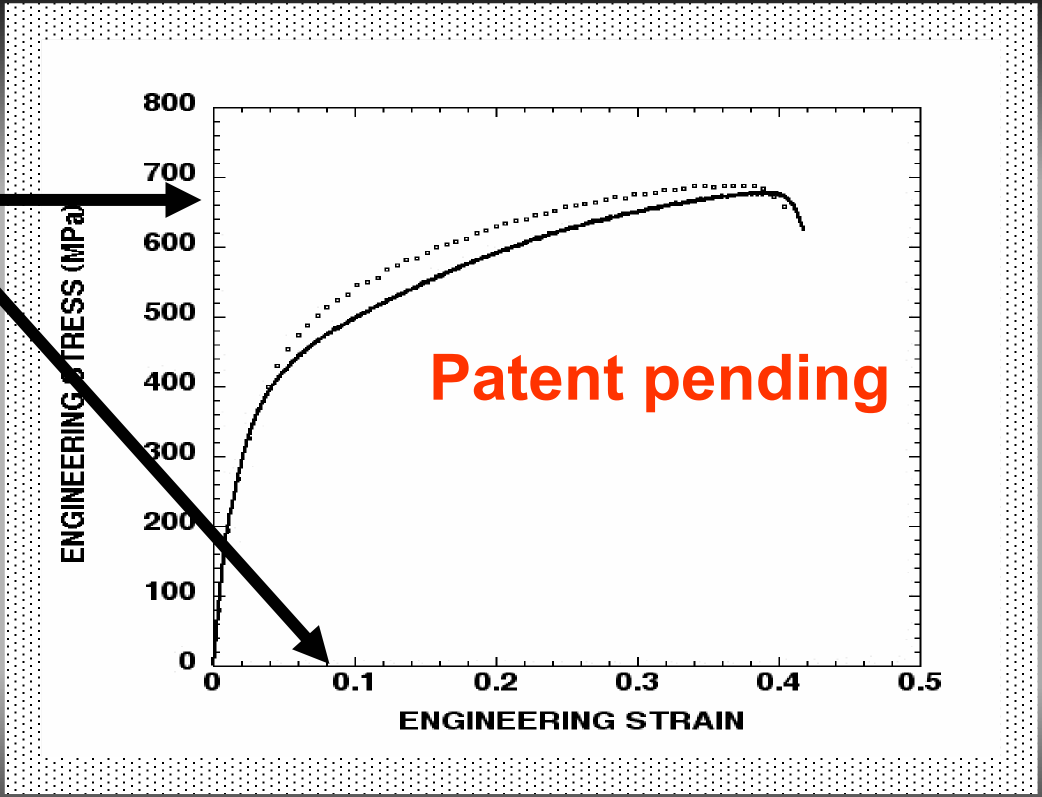
surface roughness:
0.736 nm (293 K – deposited $AlMgB_{14}$ film)
0.171 nm (573 K-deposited $AlMgB_{14}$ films)

Y. Tian , A. F. Bastawros, C. C. H. Lo, A. P. Constant, A. M. Russell, and B. A. Cook, "Superhard, self-lubricating $AlMgB_{14}$ films," Submitted to Appl. Phys. Lett.

Binder phase:

- metal-based binders are needed to enable thermal spray of ceramic coatings
- binder materials increase toughness, enable liquid phase sintering to full density

Co, 99.9% purity, cold-worked



Binder phase:

Hardness and Fracture Toughness
as Estimated by the Palmqvist Technique
(1 Kg load)

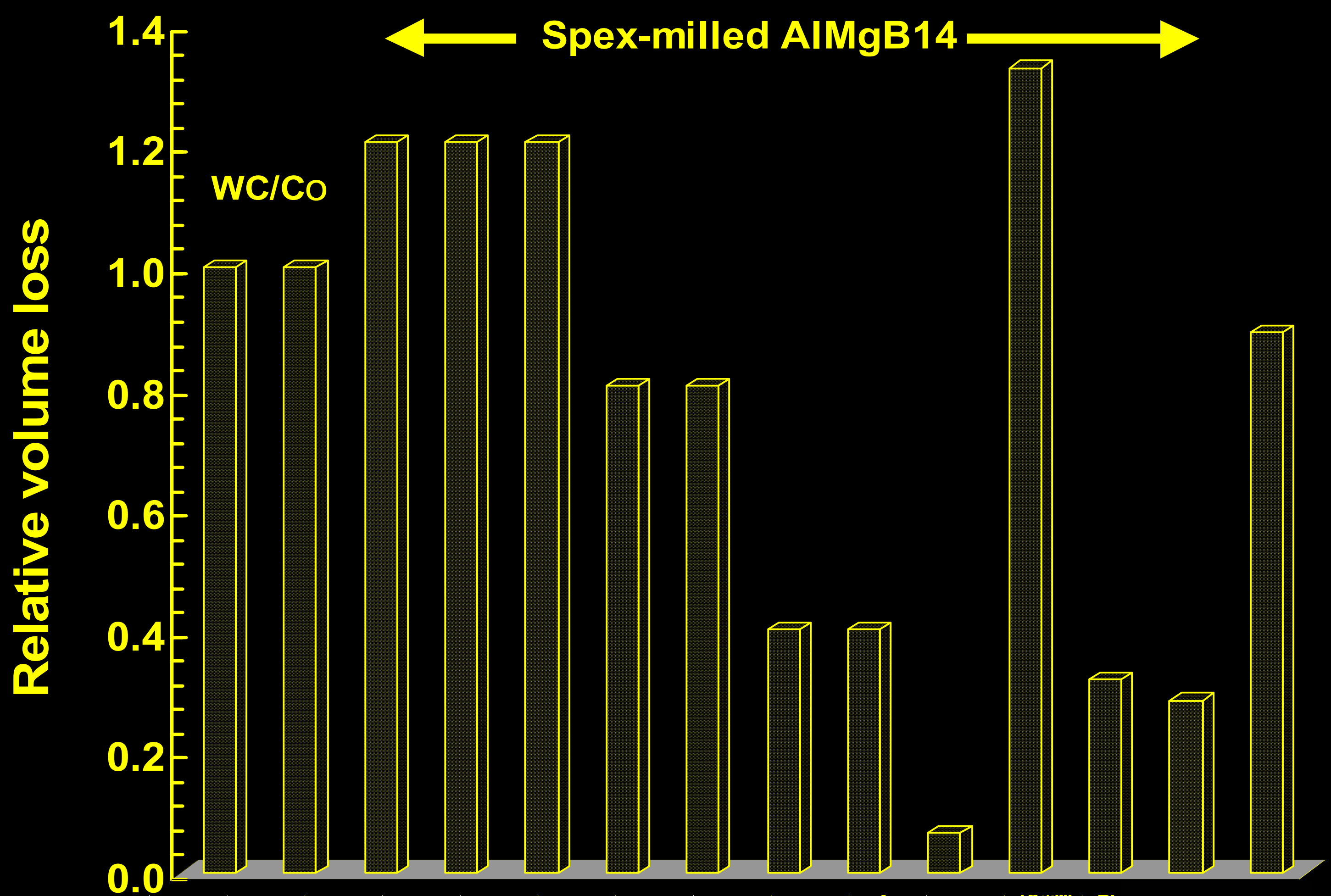
Material	Hardness (GPa)	K_{IC}, (MPa√m)
SiC	23	3.0
WC/Co (1)	22 – 13	5 - 10
$AlMgB_{14}$ (baseline)	30	3 - 4
$AlMgB_{14}$ + 5 vol % binder	28	4.2 – 6.3
$AlMgB_{14}$ + 20 vol % binder(2)	25	6.6 – 8.5

(1) Hardness and fracture toughness of WC/Co depend strongly on the amount of Co present. Typical amounts range from 6 to 25 volume percent.

results of recent consolidation studies on the baseline $AlMgB_{14}$ show that a hardness of 30 GPa combined with a K_{1c} of 10 MPa√m is achievable

Abrasion resistance: *Spex-milled* materials

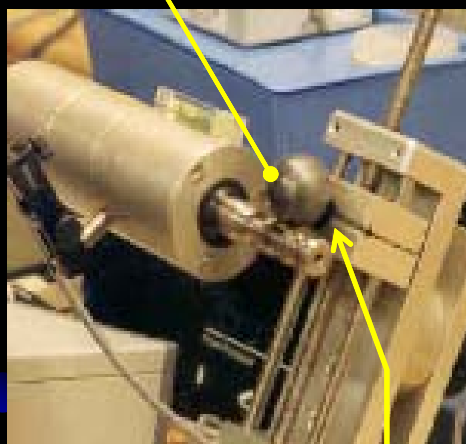
2-body abrasion - high velocity alumina particle flux



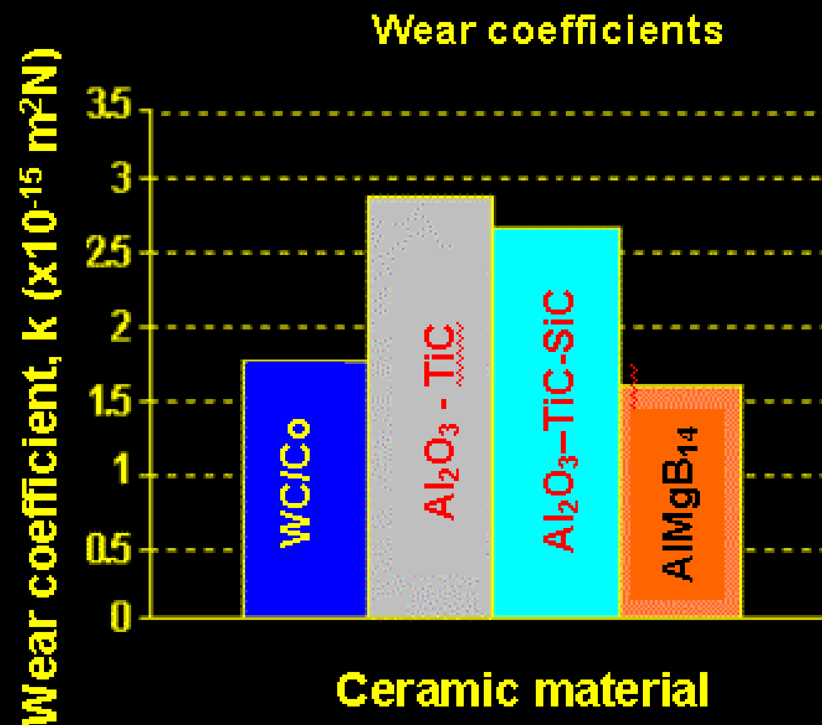
Wear resistance:

Calo 3-body Abrasive Wear Test

Cemented Carbide Ball



Tool Material



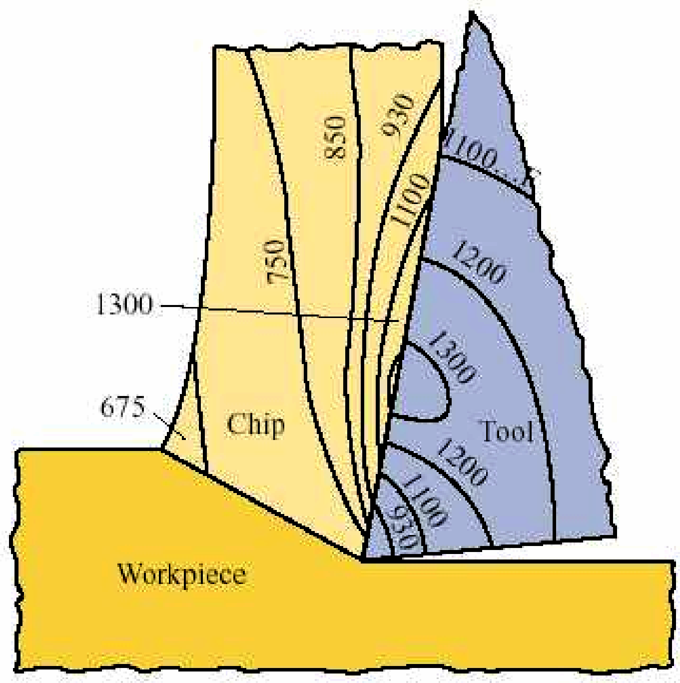
Archard's Equation: $k \propto b^4$

k : Wear Coefficient

b : Crater Diameter

Chemical stability:

high temperature diffusion / chemical reactivity



- Local temperatures can reach 1300°C during high speed machining
- Diffusion & dissolution lead to rapid wear and reduced efficiency
- Thermal issues become more acute for Ti, Ti alloys

- chemical stability with respect to workpiece

High temperature diffusion:

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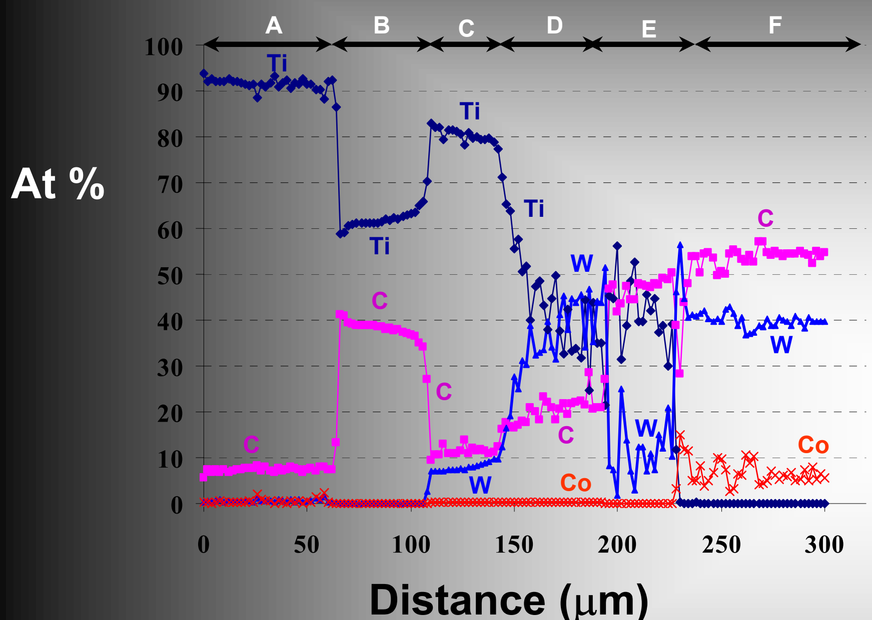
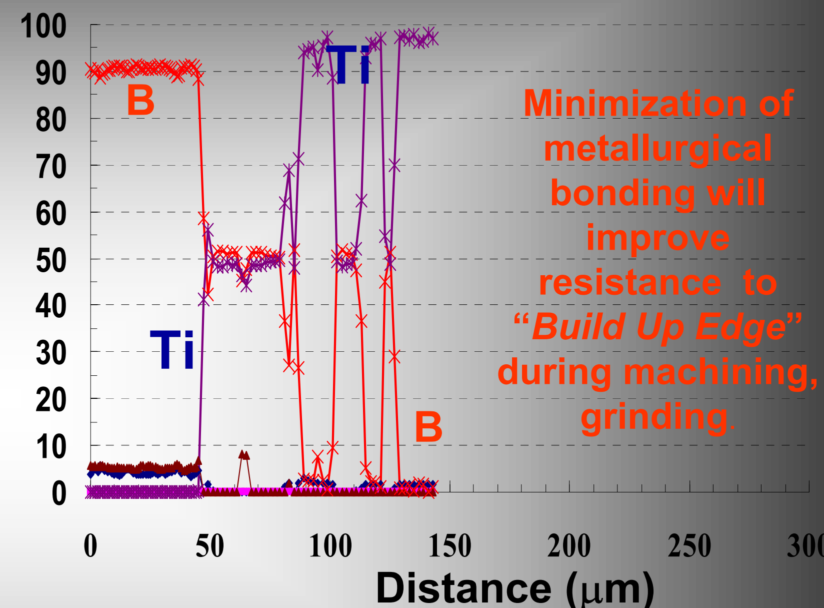
120 hours at 1273K

Ti vs. WC-Co



Ti vs. $AlMgB_{14}$



Diffusion Zone Widths:

WC-Co + Ti → 200 μm Strong Interfacial Reaction

$AlMgB_{14}$ + Ti → 120 μm Absence of Interfacial Reaction

$AlMgB_{14}$ shows lower diffusive reactivity than WC/Co when evaluated against titanium

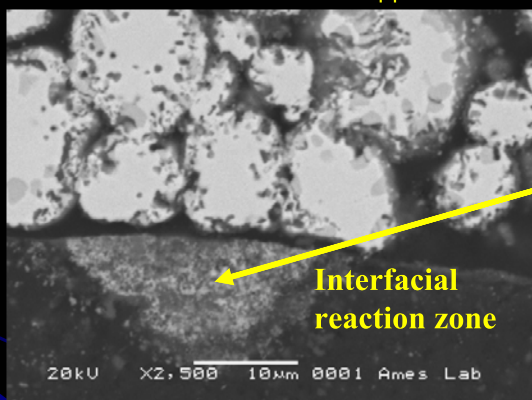
Chemical stability:

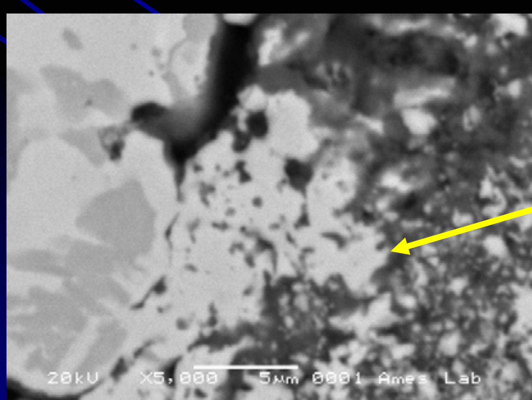
high temperature chemical reactivity / oxidation resistance

Identification and optimization of reactivity with engineered matrix materials

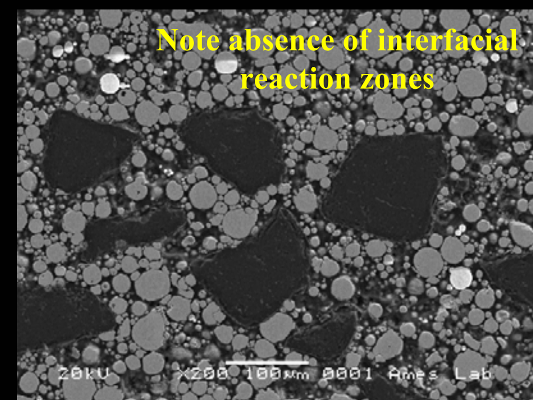
Reactivity test: 8 hours at 1353K in ambient air

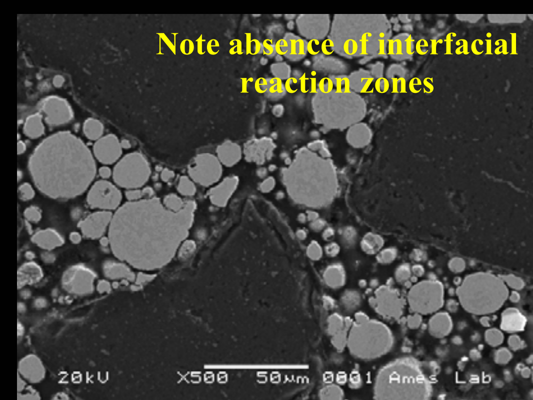
Range of interest: 900°C to 1300°C
Diffusive reactions observed with baseline $AlMgB_{14}$





Modified composition (derived from $AlMgB_{14}$ parent) shows negligible reactivity under identical conditions





Relevance to IMF program

Implementation of $AlMgB_{14}$-based materials projected to result in a total energy savings of 10 - 15 Tbtu/yr.

Potential markets

1) Current estimated annual cubic boron nitride market:

Cubic BN: reference cost $1,500/ #

Region	Company	% of global market	# produced	$ value
Domestic:	GE	36%	80,000	~120M
Europe:	DeBeers	36%	80,000	~120M
Japan/Pacific Rim:	Showa Denko	27%	60,000	~90M
Global totals:		100%	220,000	$330M

- ~ 1/4 of domestic CBN mkt. ⇒ $30M

2) Penetration into existing diamond market

3) "Upgrade" of current tungsten-carbide users

- 20% of current annual sales ($1.3B) ⇒ $260M

4) Other markets:

- (woodworking, mining, paper pulping, friction stir welding)

5) Protective coatings

- (agriculture, mining, construction, medical,…)

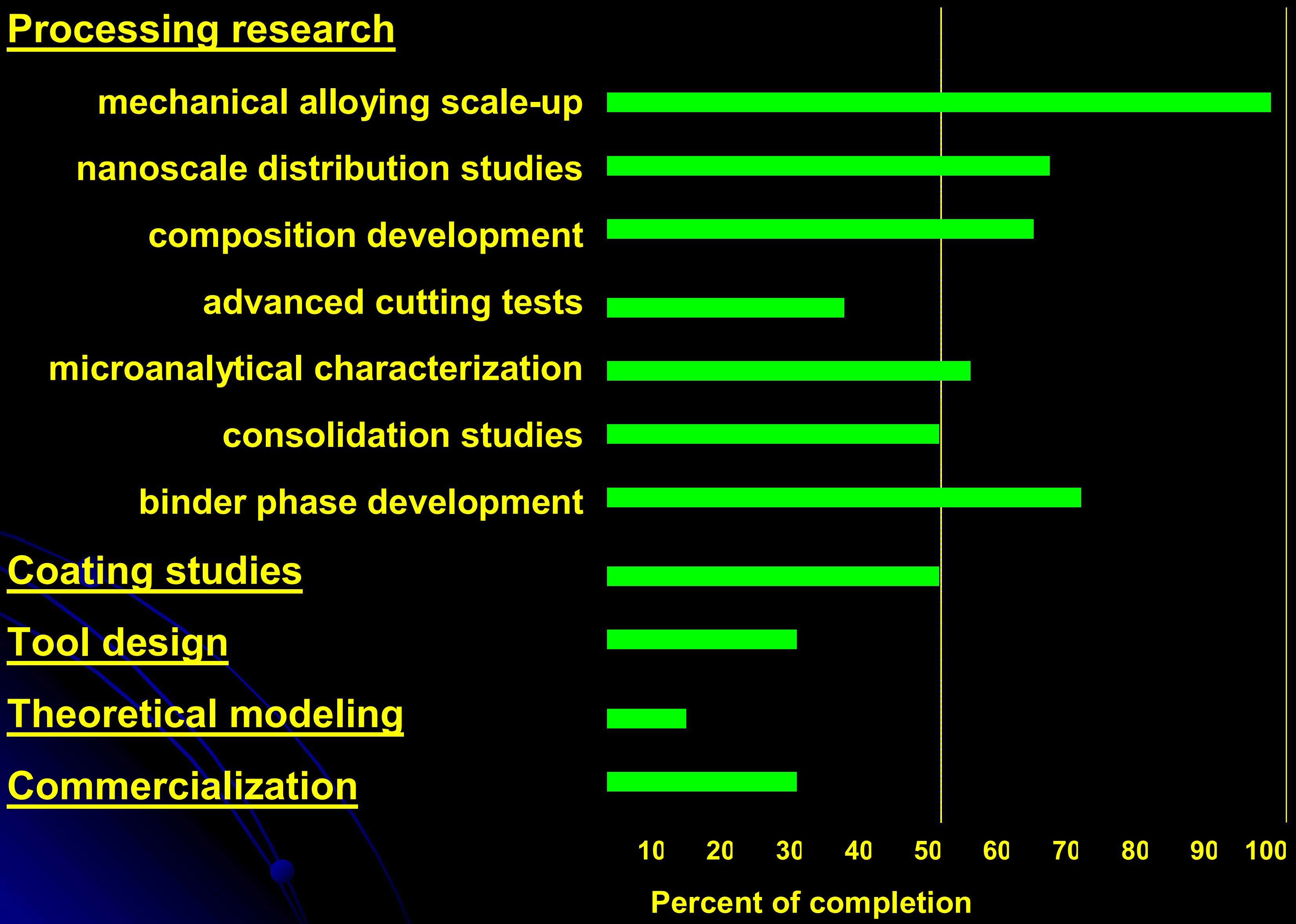
Anticipated contribution of knowledge:

- **Improved understanding of fundamental mechanisms responsible for extreme hardness**
    - role of Hall-Petch relationship in composites
    - contribution of dislocation motion to microplasticity in B_{12} compounds
    - limits to hardness (strength) in nanocomposites
    - relationship between hardness and electrical/thermal conductivity
    - high temperature stability of nanocomposites
- **Improved ceramic processing technology**
    - solid state mechanosynthesis - reduced sintering temperatures
    - densification mechanisms
    - binder phase - interfacial chemistry
- **Development of advanced thin film coatings**
    - congruent ablation vs. sputtering vs. thermal spray
    - tribological properties - ultra low friction

Commercialization roadmap:

- Viable Technologies, LLC has signed an option agreement for baseline technology, advanced compositions, and binder
- 3-way partnership (Viable, ISURF, research team) to assist industrial partners on identification of potential opportunities, optimization of properties, and transfer of samples for evaluation and feedback.
- Development of formal business plan is in progress; completion expected August - September ‘03.
- Pilot plant start-up expected second quarter, FY’04

Milestone schedule:



Publications:

Y. Tian, A. Constant, C.H.C. Lo, J.W. Anderegg, A.M. Russell, J.E. Snyder, and P. Molian, "Microstructure Evolution of Al-Mg-B Thin Films by Thermal Annealing", Journal of Vacuum Science and Technology A, submitted (under review).

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V. Bedekar, D. Bhat, S. Batzer, and L. Walker, "CHEMICAL INTERDIFFUSION STUDY OF ULTRA-HARD CERAMIC $AlMgB_{14}$ IN THE MACHINING OF AEROSPACE ALLOYS," Presented at GREAT INTERNATIONAL SOUTHWEST REGION X GRADUATE STUDENT TECHNICAL CONFERENCE (GSTC), March 28-29, 2003, Houston, Texas

Patents - Disclosures:

Provisional Utility Patent Serial No. 60/422,001, “Ductile Binder Phase for Use with $AlMgB_{14}$ and Other Hard Ceramic Materials "; B.A. Cook, A.M. Russell, and J.L. Harringa (ISURF #2949, filed October 29, 2002).

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Intellectual Property Disclosure and Record, filed August, 2002, “ A New, Oxidation Resistant, Ultra-hard Material, Aluminum Chromium Boride, $AlCrB_{14}$"; B.A. Cook, A.M. Russell, and J.L. Harringa. (ISURF docket number 2951, AL484).

Intellectual Property Disclosure and Record, filed August, 2002, “ A New, Oxidation Resistant, Ultra-hard Material, Aluminum Titanium Boride, $AlTiB_{14}$"; B.A. Cook, A.M. Russell, and J.L. Harringa. (ISURF docket number 2950, AL483).

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